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(54) **Membranes for aromatics/saturates separation.**

(57) The present invention describes a method for separating mixtures of aromatics and non-aromatics by permeation through a sulfonated polysulfone membrane which is selective for aromatics.

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The use of membranes to separate aromatics from saturates has long been pursued by the scientific and industrial community and is the subject of numerous patents.

U.S. Patent 3,370,102 describes a general process for separating a feed into a permeate stream and a retentate stream and utilizes a sweep liquid to remove the permeate from the face of the membrane to thereby maintain the concentration gradient driving force. The process can be used to separate a wide variety of mixtures including various petroleum fractions, naphthas, oils, hydrocarbon mixtures. Expressly recited is the separation of aromatics from kerosene.

U.S. Patent 2,958,656 teaches the separation of hydrocarbons by type, i.e. aromatic, unsaturated, saturated, by permeating a portion of the mixture through a non-porous cellulose ether membrane and removing permeate from the permeate side of the membrane using a sweep gas or liquid. Feeds include hydrocarbon mixtures, e.g., naphtha (including virgin naphtha, naphtha from thermal or catalytic cracking, etc.).

U.S. Patent 2,930,754 teaches a method for separating hydrocarbons, e.g., aromatic and/or olefins from gasoline boiling range mixtures, by the selective permeation of the aromatic through certain non-porous cellulose ester membranes. The permeated hydrocarbons are continuously removed from the permeate zone using a sweep gas or liquid.

U.S. Patent 4,115,465 teaches the use of polyurethane membranes to selectively separate aromatics from saturates via pervaporation.

The present invention relates to a process for the separation of aromatics from saturates by using a membrane. Compared to distillation, membrane permeation can lead to considerable energy savings. A membrane can separate a mixture of aromatics and saturates, e.g., a heavy cat naphtha, into a high-octane, mainly aromatic permeate and a high-cetane, mainly saturated retentate. Both permeate and retentate are more valuable than the starting heavy cat naphtha.

The present invention is a method for separating mixtures of aromatics and non-aromatics into aromatic-enriched and non-aromatic-enriched streams by contacting the aromatics/non-aromatics mixture with one side of a sulfonated polysulfone membrane, and selectively permeating the aromatic components of the mixture through the membrane.

Polysulfones are commercially available. Examples are Bisphenol-A polysulfone such as Udel (trade mark - available from Amoco) and polyether-sulfone such as Victrex (trade mark - available from ICI). Several patents and publications describe the sulfonation of polysulfones, e.g. U.S. 3,875,096, U.S. 4,625,000, U.S. 3,709,841, Noshay and Robeson, *J. Appl. Polym. Sci.*, 20, 1885 (1976), O'Gara et al., *J. Polym. Sci. Part B, Polym. Phys.* 25, 1519 (1987), and Johnson et al., *J. Polym. Sci., Polym. Chem. Edn.*, 22, 721 (1984).

The membranes are useful for the separation of aromatics from saturates in petroleum and chemical streams, and have been found to be particularly useful for the separation of large substituted aromatics from saturates as are encountered in heavy cat naphtha streams. Other streams which are also suitable feed streams for aromatics from saturates separation are intermediate cat naphtha streams boiling at 93-160°C, light aromatics content streams boiling in the C₅-150°C range, light catalytic cycle oil boiling in the 200-345°C range as well as streams in chemical plants which contain recoverable quantities of benzene, toluene, xylenes (BTX) or other aromatics in combination with saturates. The separation techniques which may successfully employ the membranes of the present invention include perstraction and pervaporation.

Perstraction involves the selective dissolution of particular components contained in a mixture into the membrane, the diffusion of those components through the membrane and the removal of the diffused components from the downstream side of the membrane by the use of a liquid sweep stream. In the perstractive separation of aromatics from saturates in petroleum or chemical streams, the aromatic molecules present in the feedstream dissolve into the membrane film due to similarities between the membrane solubility parameter and those of the aromatic species in the feed. The aromatics then permeate (diffuse) through the membrane and are swept away by a sweep liquid which is low in aromatics content. This keeps the concentration of aromatics at the permeate side of the membrane film low and maintains the concentration gradient which is responsible for the permeation of the aromatics through the membrane.

The sweep liquid is low in aromatics content so as not to itself decrease the concentration gradient. The sweep liquid is preferably a saturated hydrocarbon liquid with a boiling point much lower or much higher than that of the permeated aromatics. This is to facilitate separation, as by simple distillation. Suitable sweep liquids, therefore, would include, for example, C₃ to C₆ saturated hydrocarbons and lube basestocks (C₁₅-C₂₀).

The perstraction process is run at any convenient temperature, preferably as low as possible.

The choice of pressure is not critical since the perstraction process is not dependent on pressure, but on the ability of the aromatic components in the feed to dissolve into and migrate through the membrane under a concentration driving force. Consequently, any convenient pressure may be employed, the lower the better to avoid undesirable compaction, if the membrane is supported on a porous backing, or rupture of the membrane, if it is not.

If C₃ or C₄ sweep liquids are used at 25°C or above in liquid state, the pressure must be increased to keep them in the liquid phase.

Pervaporation, by comparison, is run at generally higher temperatures than perstraction and relies on vacuum on the permeate side to evaporate the permeate from the surface of the membrane and maintain the concentration gradient driving force which drives the separation process. As in perstraction, the aromatic molecules present in the feed dissolve into the membrane film, migrate through said film and emerge on the permeate side under the influence of a concentration gradient. Pervaporation separation of aromatics from saturates can be performed at a temperature of about 25°C for the separation of benzene from hexane but for separation of heavier aromatic/saturate mixtures, such as heavy cat naphtha, higher temperatures of at least 80°C and higher, preferably at least 100°C and higher, more preferably 120°C and higher should be used. Temperatures of about 210°C have been successfully used with sulfonated polysulfone membranes of the present invention, the maximum upper limit being that temperature at which the membrane is physically damaged. Vacuum on the order of 1-50 mm Hg is pulled on the permeate side. The vacuum stream containing the permeate is cooled to condense out the highly aromatic permeate. Condensation temperature should be below the dew point of the permeate at a given vacuum level.

The membrane itself may be in any convenient form utilizing any convenient module design. Thus, sheets of membrane material may be used in spiral wound or plate and frame permeation cell modules. Tubes and hollow fibers of membranes may be used in bundled configurations with either the feed or the sweep liquid (or vacuum) in the internal space of the tube or fiber, the other material obviously being on the other side.

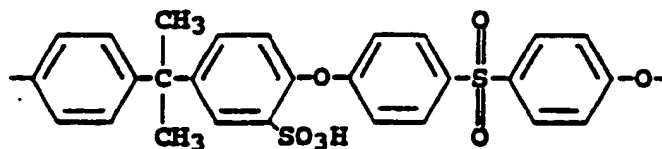
When the membrane is used in a hollow fiber configuration with the feed introduced on the exterior side of the fiber, the sweep liquid flows on the inside of the hollow fiber to sweep away the permeated highly aromatic species, thereby maintaining the desired concentration gradient. The sweep liquid, along with the aromatics contained therein, is passed to separation means, typically distillation means, however, if a sweep liquid of low enough molecular weight is used, such as liquefied propane or butane, the sweep liquid can be permitted to simply evaporate, the liquid aromatics being recovered and the gaseous propane or butane (for example) being recovered and reliquefied by application of pressure or lowering of temperature.

Sulfonated polysulfone films can be obtained by preparing a solution in a suitable solvent, e.g. dimethylformamide, casting on a glass plate or a porous support, adjusting the thickness with a casting knife and drying the membrane first at room temperature, then at high temperature, e.g., 120°C.

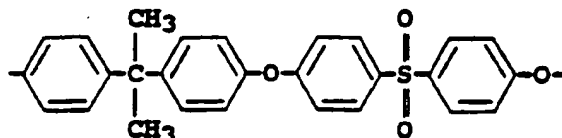
Ion exchange can be effected by immersing a membrane, in which the sulfonic groups are neutralized by a metal ion, e.g. Na⁺, in the solution of a hydroxide or salt of a second metal, e.g. Ag or Cd. If the Na⁺ form is immersed in a Cr(NO₃)₃ solution, the H⁺ form is obtained.

In the following examples which illustrate the invention, membranes were used to separate aromatics from saturates in a pervaporation apparatus. The pervaporation apparatus was a cell, separated into two compartments by a porous metal plate, on which the membrane was supported. During a pervaporation experiment the aromatics/saturates mixture was circulated through the upper compartment at the desired temperature. The lower compartment was kept at reduced pressure. The permeate was collected in a trap cooled with dry ice-acetone or dry ice-isopropanol and periodically analyzed by gas chromatography. The feed contained 20 weight % isooctane, 10% toluene, 30% n-octane and 40% p-xylene.

The sulfonated polysulfone used to prepare the membranes described in the following examples was made according to U.S. 3,875,096. Elemental analysis gave 9.35 wt%S and 1.31 wt% Na. We calculated that 47 weight % of the repeat units corresponded to the formula



and 53 weight % of the repeat units corresponded to the non-sulfonated formula



2/3 of the $-\text{SO}_3\text{H}$ groups were neutralized with Na.

The effectiveness of the separation was measured by determining the separation factor using toluene. This separation factor is defined as follows:

$$\text{Separation Factor} = \frac{\text{Ratio of toluene to n-octane in permeate}}{\text{Ratio of toluene to n-octane in feed}}$$

Example 1

20 g of sulfonated polysulfone in the sodium form, described above, was dissolved in 80 g of dimethylformamide. The solution was cast on a glass plate, adjusting the thickness with a casting knife. The membrane was dried first at room temperature, then at 110°C in vacuum for 3 hours.

The film so obtained was used to separate aromatics from saturates in a pervaporation experiment described above. The following table gives the results.

| Temperature °C | Separation Factor For Toluene/n-Octane | Normalized Flux (Kg M/M ² /D) |
|-------------------|---|---|
| 150 | 12 | 30 |
| 170 | 11.5 | 110 |
| 190 | 9.5 | 290 |

Example 2

A sulfonated polysulfone membrane in the sodium form was immersed in a 0.25 M solution of AgNO_3 and left there with slow agitation for 64 hours. The membrane was washed in water and dried in an oven at 120°C for 2 hours. Analysis showed that the membrane contained 8.3 weight % Ag and 0.03% Na, i.e. nearly complete exchange occurred.

The following table shows the results of a pervaporation experiment.

| Temperature °C | Separation Factor For Toluene/n-Octane | Normalized Flux (Kg M/M ² /D) |
|-------------------|---|---|
| 170 | 13 | 35 |
| 190 | 11 | 215 |
| 210 | 8.6 | 650 |

Example 3

A sulfonated polysulfone membrane, in the sodium form, was immersed in a 0.25 M solution of CdCl_2 and left there with slow agitation for 64 hours. The membrane was washed with water and dried at 120°C for 2 hours. Analysis showed that the membrane contained 4.6 weight % Cd and 0.08 weight % Na, i.e. nearly complete exchange occurred.

The following table shows the results of a pervaporation experiment.

| Temperature °C | Separation Factor For Toluene/n-Octane | Normalized Flux (Kg M/M ² /D) |
|-------------------|---|---|
| 190 | 13 | 35 |
| 210 | 11.3 | 95 |

Example 4

A sulfonated polysulfone membrane in the sodium form was immersed in a 0.25 M solution of $\text{Cr}(\text{NO}_3)_3$ and left there with slow magnetic agitation for 2 days. Then the membrane was rinsed with water for an hour and dried at 120°C for 2 hours. Elemental analysis gave 0.13% Na and 0.005% Cr, i.e. most sodium had been displaced, but very little Cr was combined with the sulfonic groups, i.e. the free acid was formed.

The following table gives the results of a pervaporation experiment described above.

| Temperature °C | Separation Factor For Toluene/n-Octane | Normalized Flux (Kg M/M ² /D) |
|-------------------|---|---|
| 170 | 14 | 110 |
| 190 | 10 | 443 |
| 210 | 6.9 | 1035 |

Example 5

A second sulfonated polysulfone membrane in the sodium form was immersed in a 0.25 M solution of $\text{Cr}(\text{NO}_3)_3$ and left there with slow magnetic agitation for 2 days. Then the membrane was rinsed with water for an hour and dried at 120°C for 2 hours. Elemental analysis gave 0.04% Na and 0.03% Cr, i.e. most sodium had been displaced, but very little Cr was combined with the sulfonic groups, i.e. the free acid was formed.

The following table gives the results of a pervaporation experiment described above.

| Temperature °C | Separation Factor For Toluene/n-Octane | Normalized Flux (Kg M/M ² /D) |
|-------------------|---|---|
| 170 | 13.8 | 73 |
| 190 | 11.2 | 282 |

Claims

1. A method for separating mixtures of aromatics and non-aromatics into aromatic-enriched and non-aromatic-enriched streams comprising:
 - a) Contacting said aromatics/non-aromatics mixture with one side of a sulfonated polysulfone membrane, and
 - b) selectively permeating the aromatic components of the mixture through the membrane.
2. The method of claim 1 wherein said membrane is obtained by casting a sulfonated polysulfone solution.
3. The method of claim 2 wherein said membrane is obtained by ion exchange, effected by immersing a first metal derivative of a sulfonated polysulfone membrane into an aqueous solution of a hydroxide or salt of a second metal.
4. The method of claim 3 wherein the first metal is sodium.
5. The method of claim 3 or 4 wherein the second metal is selected from the group consisting of Ag, Cd, and Cr.
6. The method of any preceding claim wherein the polysulfone is aromatic.
7. The method of any preceding claim wherein the polysulfone is derived from Bisphenol-A.
8. The method of any preceding claim wherein the separation is performed under pervaporation conditions.

9. The method of any of claims 1 to 7 wherein the separation is performed under perstraction conditions.
10. The method of any preceding claim wherein the aromatics/non-aromatics mixtures are selected from heavy cat naphtha streams, intermediate catalytic naphtha streams, light aromatics streams boiling in the C₅-150°C range and light catalytic cycle oils boiling in the 200-345°C range.

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EUROPEAN SEARCH REPORT

Application Number

EP 91 30 6246

| DOCUMENTS CONSIDERED TO BE RELEVANT | | | |
|--|---|--|--|
| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | CLASSIFICATION OF THE APPLICATION (Int. Cl.5) |
| D,A | US-A-3 875 096 (A.F. GRAEFE et al.) * abstract * | 1-7 | B 01 D 61/36 B 01 D 71/68 C 10 G 31/11 C 07 C 7/144 |
| P,A | US-A-5 019 666 (G. SARTORI et al.) * claims 1,7-9 * | 1,8-10 | |
| A | EP-A-0 165 077 (NITTO ELECTRIC INDUSTRIAL CO) * claims * | 1-7 | |
| A | GB-A-1 376 185 (AGENCE NATIONALE DE VALORISATION DE LA RECHERCHE) * claims 1,23,24 * | 1 | |
| | | | TECHNICAL FIELDS SEARCHED (Int. Cl.5) |
| | | | B 01 D C 10 G C 07 C |
| The present search report has been drawn up for all claims | | | |
| Place of search BERLIN | | Date of completion of the search 11-08-1992 | Examiner CORDERO ALVAREZ M. |
| <p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p> | | | |

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